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The Atomic Weight of Zinc
as determined
by the composition of the Oxide.

A Dissertation
for the degree of Doctor of Philosophy
at the
Johns Hopkins University,
by
William M. Burton.
1889.

54.331

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I. Introduction and Historical Statement.

The accurate determination of the atomic weight of zinc has been beset by three difficulties, 1st, in regard of obtaining the metal in a pure condition; 2d, that of obtaining well crystallized and stable compounds of constant composition; 3rd, the inexactness of the methods of determining zinc in its compounds. Further, the use of platinum vessels, as will be seen, may have been a frequent cause of unreliable results.

The methods which have been employed are:

1. The conversion of the metal into oxide and then by ignition into oxide. (Berzelius, Berzelius, Jacquelain and Erdmann.)

2. The conversion of the metal into sulphate and then by ignition into oxide. (Jacquelain and Baubigny.)

3. Solution of the metal in acid and the

measurement of the hydrogen. (Gay Lussac, Van der Plaats, and Reynolds and Ramsay.)

4. Solution of the metal in acid and combustion of the hydrogen. (Favre).

5. Ignition of the oxalate with combustion of the carbon monoxide and determination of the oxide of zinc and the whole of the carbon dioxide. (Favre.)

6. Analysis of the double chloride of zinc and potassium, with a determination of the zinc and chlorine. (Marignac.)

The following contains a brief statement of the results, arranged in chronological order, which have been hitherto obtained.

1809. Gay Lussac. Memoir d'Arcueil 2. 174.

Method.- Conversion of the metal into nitrate and thence into oxide; decomposition of the nitrate and measurement of hydrogen.

100 parts of zinc, by weight, gave 124·41 parts of oxide.

O : Zn = 1 : 4·0 9 7; Accordingly if the Atomic weight of oxygen = 100, that of zinc

Atomic weight of oxygen = 10, that of zinc = 65·52

" " " " = 15·91 " " " = 6·5·34

811. Berzelius. - Gilbert's Annalen 37-4·10.

Mutual Conversion of the metal into oxide

and then into oxide. The metal was redistilled

but contained small quantities of Lead and

sulphur which could not be removed.

100 parts, by weight, of zinc gave 124·4 parts of oxide

O : Zn = 1 : 4·098 - Hence if the

Atomic weight of oxygen = 100, that of zinc = 409·8

" " " " = 16, " " " = 65·57

" " " " " " 5·41

826(?) Berzelius, (Pogg. Annalen 8, 184.) states that according

to the concordant results of Gay Lussac and

himself, 100 parts by weight of zinc yield 124·8

parts of oxide. - O : Zn = 1 : 4·032, Hence if the

Atomic weight of Oxygen = 100, that of zinc 403·23

" " " " 16, " " 64·52

[illegible] - Comptes Rendus 1842, 630. Journal für [illegible]

Methods – 1st. Conversion of metal into nitrate and then by ignition into oxide. 2d. Conversion of metal into sulphate and then by ignition into oxide. Two determinations [illegible] each [illegible]. The zinc was distilled in a current of hydrogen, but contained a small quantity of lead for which the results were corrected. The [illegible] were [illegible] in a [illegible] crucible. The oxides were found to be free from nitrogen and sulphur. By the first method 100 parts of zinc (9·917 and 9·809 grams) gave 124·178 and 124·172 (12·3138 and 12·18 grams) of oxide. – O : Zn 2·3908 : 9·917 = 1 : 4·1437.

O : Zn = 2·371 : 9·809 = 1 : 4·1371. Hence if the [illegible] weight of oxygen = 100, that of zinc = $\left\{\begin{matrix}413{\cdot}76\\413{\cdot}71\end{matrix}\right\}$ 413·74

" " " " = 16 " " " $\left\{\begin{matrix}66{\cdot}20\\66{\cdot}19\end{matrix}\right\}$ 66·20

" " " " = 16 " " " $\left\{\begin{matrix}66{\cdot}04\\66{\cdot}03\end{matrix}\right\}$ 66·04

the influence which the hypothesis of Prout had acquired through the efforts of Dumas. Four determinations by the first method gave

$ZnO : 2CO_2 = 7{\cdot}790 : 8{\cdot}265 = 1 : 1{\cdot}0730.$

" : " = 7·342 : 7·883 = 1 : 1·0737

" : " = [illegible] : 918 = 1 : [illegible]11

" : " = [illegible] : [illegible] = 1 : 1[illegible]1.

Hence " : " = 4·0018 : 25·784 = 1 : 1[illegible].

Hence if O = 100, and C = 75, Z_N = 412·6 (max. 413·4, min 412·3)

" O = 16, " C = 12, Z_N = 6602 (max. 6614, min 6597).

" O = 15·96 " C = 11·97, Z_N = 6585 (max. 6598, min 6580)

Three determinations by second method gave.

$Z_N : H_2O = 25{\cdot}389 : 6{\cdot}928 = 1 : 0{\cdot}27287.$

" : " = 30·369 : 8·297 = 1 : 0·27321.

" : " = 31·776 : 8·671 = 1 : 0·27288.

Whence $Z_N : H_2O$ = 87·534 : 23·896 = 1 : 0·27298.

Hence if C = 100, and H = 12·5, Z_N = 412·1 (max. 412·3, min 411·9)

" O = 16, " H = 1, Z_N = 6594 (max. 6597, min 6590)

" O = 15·96 " H = 1, Z_N = 65·77 (max. 65·81, min 65·73).

1843. Axel Erdmann - Liebig's Annalen 50 433

Method - Conversion of the metal into the nitrate and then into oxide. The metal was prepared by reducing the pure oxide with charcoal obtained from sugar, and distilling in a current of hydrogen. The solution of the zinc and the drying and ignition of the nitrate were effected in porcelain crucibles; Erdmann having observed that, when the oxide of zinc is ignited on platinum, there is loss in [illegible] with what appears to be an alloy of platinum [illegible]. The work was undertaken at the suggestion of Berzelius who doubted the [illegible] of [illegible]. Four determinations gave.

$Zn : ZnO = 1 : 1{\cdot}24615$
$\quad " \quad : \quad " \quad = 1 : 1{\cdot}24594$
$\quad " \quad : \quad " \quad = 1 : 1{\cdot}24591$
$\quad " \quad : \quad " \quad = 1 : 1{\cdot}24573$

$\Big\}\ Zn : ZnO = 1 : 1{\cdot}24575$

By the second method 100 parts of zinc (2·398 and 3·197 grams) gave 124·15 and 124·11 (2·978 and 3·968 grams) of oxide.

$C : Zn = 0{\cdot}580 : 2{\cdot}398 = 1 : 4{\cdot}13345$

$C : Zn = 0{\cdot}771 : 3{\cdot}197 = 1 : 4{\cdot}14655$ Hence if the

Atomic weight of oxygen = 100 that of zinc = $\left\{\begin{matrix}413{\cdot}45\\414{\cdot}65\end{matrix}\right\}$ 414·00.

" " " " = 16 " " " = $\left\{\begin{matrix}66{\cdot}15\\66{\cdot}35\end{matrix}\right\}$ 66·25

" " " " = 15·96 " " " = $\left\{\begin{matrix}65{\cdot}99\\66{\cdot}18\end{matrix}\right\}$ 66·0,

1843 Favre. Annales de Chimie et de Physique (3) 10, 163.

[illegible] combustion of the carbon monoxide, and the determination of both the oxide of zinc and the total carbon dioxide. 2d. Solution of [illegible] in sulphuric acid and analysis of the hydrogen, and determination of the water produced. The zinc in the latter case contained a little lead but this was collected, weighed and subtracted from the weight of the original material.

[illegible]

$ZnO : O = 4{\cdot}06241 : 1$
" : " = 4·06519 : 1
" : " = 4·06649 : 1
" : " = 4·06947 : 1
} $Zn O : O = 4{\cdot}06591 : 1$

Hence if $O = 100$, $Zn = 406{\cdot}591$ (max. 406·947, min. 406·249).
" $O = 16$, $Zn = 65{\cdot}06$ (max. 65·11, min. 65·00).
" $O = 15{\cdot}96$ $Zn = 64{\cdot}89$ (max. 64·95, min. 64·84).

1885 Lorenzen. (Comptes Rendus, 101, 22, 1885, Chemical News, 53, 144)
Method. Ignition of the pure sulphate at the temperature of melting zinc.

6·699 grams sulphate gave 3·377 grams oxide,
8·770 " " " 4·4245 " " ,

Hence if $O = 16$, and $S = 32{\cdot}074$, $Zn = \{65{\cdot}40 / 65{\cdot}42\} = 65{\cdot}41$.
" $O = 16$, " $S = 32{\cdot}00$, $Zn = \{65{\cdot}32 / 65{\cdot}34\} = 65{\cdot}33$.
" $O = 15{\cdot}96$ " $S = 31{\cdot}98$, $Zn = \{65{\cdot}22 / 65{\cdot}24\} = 65{\cdot}23$.

1883 Marignac. Archives des Sciences Physiques et Naturelles (3) 10, 193.
Method - Analysis of the double chloride of zinc and potassium with determination of the zinc and chlorine, the latter volumetrically. The

salt was crystallised from a solution containing a slight excess of zinc chloride, since, otherwise, the salt suffered partial dissociation. The following results were obtained in a series of five determinations.

I. Salt = 2·615 Cl found 1·3011 49·755 %

" = 2·3285 ZnO " 0·6775 = 29·10 "

II. Salt = 2·6785 Cl " = 1·3323 = 49·741 %

" = [illegible] ZnO " = 1·1565 = 28·90 %

III. Salt = [illegible] Cl " = 1·3356 = 49·711 } 49·712

" = [illegible] " " = [illegible] = 1·1714 }

" = 4·017 ZnO " = 1·1615 = 28·914

IV. Salt = 2·675 Cl " = 1·3307 = [illegible] } 49·748

" = [illegible] " " = [illegible] = 1·1741 }

" = 4·0[illegible]5 ZnO " = [illegible] = 29·1[illegible] }

" = 4·8350 " " = 1·4048 = 29·084 } 29·11

V. Salt = 2·6455 Cl " = 1·3159 = 49·740 }

" = 4·0455 " " = 2·0118 = 49·731 } 49·[illegible]

" = 4·0[illegible]5 ZnO " [illegible] = [illegible] }

" = 4·0015 " " = [illegible] = 29·[illegible] } 29·[illegible]

These results would give for the atomic weight of zinc calculated on the basis of both the oxide and the chlorine.

$\{C=16, K=39{\cdot}137, Cl=35{\cdot}457\}$	$\{O=15{\cdot}96, K=39{\cdot}03, Cl=35{\cdot}37\}$
65·26	65·10
65·21	65·06
65·17	65·21
65·31	65·15
65·28	65·12
Mean 65·29	Mean 65·13

The following series of three determinations gave somewhat higher numbers, if the atomic weight is calculated on the basis of the chlorine alone.-

I. Salt = 4·2935, Cl - found = 2·1334 = 49·690 } 49·6997
" = 3·6495, " " = 1·5142 = 49·708 }
" = 3·3230 Zn_2O " = 0·9445 = 28·423 %

II Salt = 4·5470, Cl " = 2·2590 = 49·682 } 49·690
" = 4·1975, " " = 2·0851 = 49·675 }
" = 3·3230 Zn_2O " = 0·9445 = 28·423 %

III. Jack. = 3·7480, Cl. found = 1·85999 · 49·690 %

" = 3·7520, ZnO " 1·0805 · 28·64 %

These results give for the atomic weight of zinc.

$\{O = 16, K = 39·137, Cl = 35·457\}$		$\{O = 15·96, K = 39·03, Cl = 35·37\}$	
65·28		65·12	
65·34		65·23	
65·32		65·16	
Mean	65·33	Mean.	65·16.

885 Van der Plaats. Comptes Rendus 100, 55.

Method. Solution of zinc in dil. chloric acid and measurement of the hydrogen. The metal was obtained partly by reduction of the oxide in a current of hydrogen and partly by Electrolysis of the sulphate.

6·6725 grams of zinc gave 1·1424 litres hydrogen.

9·1271 " " " " 1·5643 " "

13·8758 " " " " 2·3767 "

According to which the atomic weight of zinc as compared with hydrogen would be 65·21, 65·14, and 65·18 - mean 65·18.

'17 - Reynolds and Ramsay, Jour. Chem. Soc. 1887, 851.
Method. - Solution of zinc in hydrochloric and sulphuric acid, and measurement of the hydrogen evolved. The metal was obtained by the electrolysis of the sulphate.

Altogether twenty-nine experiments were made. Out of this number four had to be rejected entirely. The first nine were not fully corrected as it was only afterwards that all the corrections necessary were understood. [illegible] The next eleven were considered only preliminary, as not all corrections were applied. Some of them were means from subsequent Experiments. The next five were carried out without any known source of error and these results are fairly concordant."

"The mean result of the eleven experiments is 65·243." "The five results considered correct are 65·5060, 65·4766, 65·4480, 65·5522, 65·4141.

Mean - 65·4987."

The following table contains a summary of the results thus far obtained:

Date.	Investigators.	At. wt. of Zn. (O = 16)	At. wt. of Zn. O = 15.96
1809	Gay Lussac	65.55	65.39
1811	Berzelius,	65.57	65.41
1826 (?)	{Berzelius / Gay Lussac}	64.53	64.35
1842	Jacquelain	{66.20 / 66.25}	{66.041 / 66.085}
1843	Favre	{65.97 / 65.95}	{65.80 / 65.78}
1845	Crämer,	65.06	64.91
1883	Dumbigney	65.41	65.23
1884	Marignac	{65.29 / 65.23}	{65.13 / 65.11}
1885.	Van der Plaats.	65.34	65.18
1887	Reynolds & Ramsay	65.64	65.45.

It having been found that zinc, in the highest state of purity and in considerable quantity, can be obtained by subjecting the metal to fractional distillation in a vacuum, it seemed desirable to [illegible]

with the elementary substance as a start-
ing [illegible] zinc, otherwise so difficult, is by this method
especially rapid and satisfactory. When the
pressure is wholly removed the zinc distills
at a temperature apparently not much above
its melting point, while the other metals
usually associated with it are, at that
temperature, very much more or very much
less volatile. Of all the methods which
have been employed for the purpose, or which
suggested themselves as feasible, the determination
by means of the oxide appeared to be the
most simple and direct; and therefore the
best provided the accuracy of the method
[illegible]. [illegible]
have been offered to this method of
determining the atomic weight of zinc:
Axel Erdmann[1] observed while heating
the oxide in a platinum crucible, that
the platinum becomes tarnished with

[1] Liebig's Annalen, Bd 50, p 38.

a blueish material supposed to be an alloy of platinum and zinc. For this reason he afterwards employed crucibles of porcelain. Much later Marignac[1] noticed that, when [illegible] in Hessian or Deville crucibles, there is a manifest distillation of zinc out of the crucible, and a constant loss in the weight of the oxide.

These phenomena Marignac ascribes to the dissociation of the oxide, and in them he finds an explanation of the somewhat low atomic weight obtained by Erdmann. Marignac also asserts that the oxide of zinc, derived from the nitrate, although heated to a temperature at which it undergoes dissociation, [illegible] that [illegible] but [illegible] constant. The [illegible] to be due, consequently, to the fact that, when the oxide which had been subjected to high temperatures, was dissolved in

[1] Archives des Sciences Phys. et Nat. 65, 10, 193.

hydrochloric acid in the presence of starch and iodide of potassium, a slight blue coloration was observed.

These two objections:-

First - That the oxide of zinc dissociates at high temperatures,

Second - That the oxide, though heated to the temperature at which it begins to dissociate, still retains oxides of nitrogen,

were carefully investigated and found to be without validity. As will be seen hereafter Marignac's supposed dissociation is in reality a phenomenon of reduction, which appears only when a flame is employed as the source of heat: while the blue color developed by dissolving the oxide in the presence of an iodide and starch was doubtless due, not to the presence of oxides of nitrogen, but rather to a reaction between the [illegible] causes for the liberation of iodine.

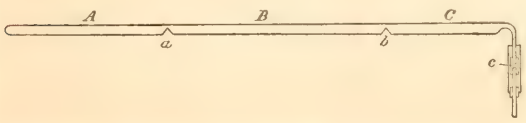
The method adopted consists in the conversion of the zinc into nitrate, the evaporation of the excess of nitric acid and the partial decomposition of the nitrate in a hot-air bath, and, finally, the ignition of the oxide to constant weight in a muffle.

I. Preparation of pure zinc.

The metal employed was that obtained from Dr. Schuchardt, of Görlitz; and was that which is designated on the labels of chemicals as "Zincum. met. absolut. chem. pur. (für forensische Zwecke)." It was found to contain a small quantity of lead and a trace of cadmium but no other impurities.

The distillation was effected in hard glass tubes of the size of those ordinarily employed in the combustion of carbon compounds. Fig I. represents one of the tubes when ready for distillation. A tube about 650 mm.

FIG. I.



in length was fused together at one end, and from 150 to 170 grams of zinc introduced. At two points a and b, the glass was softened in the flame of the blast lamp and depressed by means of a red-hot file, thus dividing the tube into [illegible] which are designated as A, B and C. The open end of the tube was then drawn out and turned down in the manner indicated. At c it was connected with a Sprengel air pump having a manometer attached. The attachment of the tube to the pump was made by means of a rubber tube firmly tied with [illegible] and sealed by mercury. The use of glycerin was found to be impracticable because of the action of the vapor of zinc upon that of glycerin, by which the oxide of zinc was formed and volatile substances were liberated whose presence rendered a high degree of Exhaustion impossible. The tube having been

thoroughly exhausted was then heated in a combustion furnace throughout nearly its whole length, but most strongly in the compartment A containing the Zinc, and least strongly in the compartment C. When raised to its fusing point the zinc begins to distill quite rapidly from A into B, and more slowly from B into C. The vapors from A condensed in B in the form of globules upon the glass, which when they had attained sufficient size ran down upon the floor of the tube, giving when cooled a thick bar of the metal having the form of the lower half of the tube. Those globules which were left upon the upper portion of the tube, when the gas was turned off, solidified into beautiful but apparently very complicated crystals, which will be considered later in this dissertation. When the metal in A had been reduced to about one fourth of the quantity originally taken, and about one

tenth of the whole had distilled into C, the distillation was suspended. The tube usually cracked on cooling, but not until the temperature had fallen so low that there was little danger of oxidation of the zinc resulting from the admission of air. The portion remaining in A and that which had collected in C were rejected. The portion collected in B was four times redistilled in the manner described. The material deposited in B during the fifth distillation was employed for the [illegible] analysis. It was carefully analysed and found to be [illegible] of [illegible] a [illegible] of [illegible].

I have examined spectroscopically [illegible]

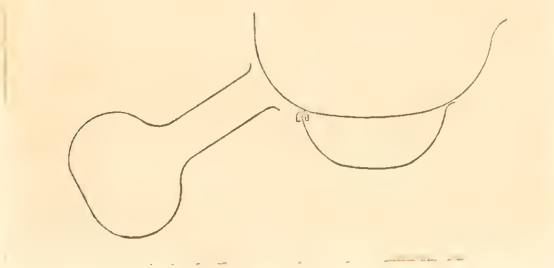
by distillation in a vacuum. The apparatus used was Prof. Rowland's induction coil, driven by a Siemens alternating dynamo, and his 20-foot concave grating mounted [illegible]. Photographs were taken in the ultra violet from W.L. 4000 to W.L. 2000, with wide slit and [illegible]. The lines are many of the strongest lines of such metals as lead, tin, [illegible] and in a specimen of so-called C.P. [illegible] several lines belonging to each of these metals were found on the negatives. [illegible] in a vacuum, however, not a trace of any of the above impurities could be found."

The crystal cubes in A and C were analysed but were found to be free from any impurities, except after the first distillation, when the contents of A contained a small amount of lead, and those of C a trace of cadmium

II. – The preparation of pure nitric acid.

It was found impossible by distilling from a platinum retort to prepare an acid which on evaporation would not leave a residue. The distillate contained in [illegible] which the acid had extracted from the solder used in joining the tube to the body of the retort. The following simple arrangement was therefore employed, Fig 2. – Two platinum dishes –

FIG. 2.



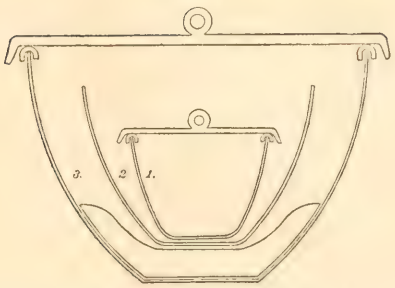
one 100 mm., the other 70 mm wide were arranged as shown in the figure, the two being kept apart by hooks of thick platinum wire hung over the edge of the lower one.

The latter one was cooled by putting into it a piece of ice. The acid, having first been treated with nitrate of silver, was then [illegible] placed that the vapors issuing from it [illegible] upon the cold surface of the upper dish. The acid thus obtained left no residue upon evaporation. It was preserved by placing the smaller dish in which it was collected, under a bell jar. To transfer it from the dish to the crucible in which the zinc was to be dissolved, a platinum spoon was used.

III. The arrangement of crucibles and mode of procedure.

Fig. 1 [illegible] the arrangement of the porcelain crucibles employed for the conversion of the metal into oxide.

Fig. 3.



1 is a small crucible (No. 00) with lid, in which the zinc is treated with nitric acid and the nitrate converted into oxide. The crucible and its lid are separated by means of hooks of platinum wire hung over the edge. This is necessary in order that the vapors of nitric acid and of the oxides of nitrogen [illegible] may be free diffusion between the inside and the outside. As the temperature to which the oxide is heated in the muffle is very high — as high, at least, as that required for the fusion of steel, and far

above that at which the glaze upon porcelain will begin to soften, it is necessary to remove the glaze from the under side of the crucible lid; otherwise the lid would be found to be firmly stuck to the [illegible] when heated to redness or over.

This removal is easily effected by means of hydrofluoric acid. 2 is a larger crucible (No. II) without lid, from the outside of which the glaze has also been removed by ammonium silicofluoride.

1 and 2 are weighed together and are not separated from the beginning to the end of the determination.

A piece of zinc weighing about one gram was broken off by wrapping the larger piece in filter paper, pressing it in a vise and prying with a pair of nut-pick tongs. When this was a fragment was selected which was

whole, uncontaminated by the iron of the tools used. The outside was then

The pair of crucibles 1 and 2 having been weighed, but previously heated in the muffle, then zinc was placed in 1 and [illegible] acid. When the metal had completely disappeared the pair was placed in a hot-air bath consisting of a large porcelain and a larger iron crucible, the space between them being filled with sand. This bath was then heated, very gently at first, afterwards more strongly, until the vapors of nitric acid and the oxides of nitrogen ceased to come off. From this bath 1 and 2 were [illegible]

No. crucible 3 has in it a carefully [illegible] upon which No. 3 rests.

It is also supplied with a lid which is somewhat raised by means of hooks of platinum wire. To prevent sticking the gauze is removed from the under side of the lid. Finally, the whole arrangement, consisting of crucibles 1, 2 and 3 was placed in a muffle and heated for three hours to a temperature as high as that required for the fusion of steel. After weighing, the oxide was [illegible] [illegible] [illegible]

detected by the agitation of the surface of the mercury. The methods of weighing by vibrations and of double weighing - that is upon both pans - were employed throughout. Each zero-point was determined by means of three series of observations, one with short, another with long and a third with medium excursions of the pointer. The weight [illegible] zero-point was not calculated from the above table of sensibility. The sensibility of the balance with the load, whatever it might be, was determined at the time of weighing, and from that the weight to be ascertained was estimated. In order to assure himself that the weighings should not be [illegible] the operator, —

having some hours beforehand closed the room, shut off the register through which the room was warmed, and lighted the lamps which were stationed above and behind his head — would determine the empty balance. After waiting an hour without moving from his place before the balance, he would again determine the zero point. For the same purpose the zero-point was always determined just before and just after each weighing. This method is believed to be [illegible] than the [illegible] placing thermometers at each end of the balance case. The weights used belonged to a set obtained from Becker Brothers. The makers were requested to use the utmost care in the [illegible] and [illegible] and [illegible].

The following table gives their relative values; one of the ten gram weights being used as the standard.

Weight	Value as standard.
10 grams	
5 "	.004998
2 "	.010001
1 "	.050000 7
.5 "	.119980
.2 "	.200002
.1 "	.499984
.05 "	.999980
.02 "	1.999980
.01 "	4.999970
10 "	10.000000
10 "	10.000 0980
20 "	20.000 0980
50 "	50.000 054

In order to adjust the [illegible]
the [illegible]

independent of the varying humidity of the atmosphere. Two crucibles were weighed by Larsen. Two crucibles of the same weight and a weight equal to the same weight, but slightly lighter, were selected and prepared in every respect like 1 and 2 to serve as a tare. The platinum hooks upon 1, and those upon the corresponding crucibles of the tare, were brought to the same weight by filing.

The weight of the tare was then brought to within less than a milligram of that of the crucibles 1 and 2 by the addition of a thin piece of platinum foil, upon a crucible of the same kind. The slight difference between the weight of the crucibles and that of the tare could then be determined by the displacement of the zero point without the use of weights. The tare were heated with nitric acid and heated in the bath and

muffle in every respect like the Crucible

in [illegible]

V. The Results

The method in its perfected form worked so smoothly that it was not necessary to discard a single determination. The following table contains the results of fifteen successive experiments:-

	wt. of zinc	wt. of ZnO	at. wt. Zn. (O = 16)	at. wt. Zn. (O = 15.96)
1	1.11616	1.38972	65.281	65.119
2	1.02423	1.27502	65.253	65.091
3	1.11628	1.38987	65.111	65.111
4	1.05760	1.31681	65.281	65.118
5	1.04801	1.30492	65.268	65.105
6	1.02457	1.27581	65.271	65.111
7	1.04181	1.29744	65.271	65.110
8	1.14413	1.44955	65.258	65.095
9	1.10711	1.34248	65.258	65.095
10	1.12952	1.40600	65.256	65.093
11	1.11100	1.38446	65.272	65.101
12	1.10211	1.36981	65.264	65.101

13	1·03148	1·28436	65·263	65·106
15	1·05508	1·31365	65·277	65·114
		Lower	65·253	65·094
		Difference	·028	·028

If we calculate the atomic weight from the sums of the quantities of zinc taken and oxide obtained as recommended by Marignac and Stuckert[1], we have:

Atomic wt. of Zinc. O = 16	Atomic wt. of Zinc. O = 15·96
65·[illegible]	65·[illegible]

If we calculate the atomic weight of zinc on the basis of 15·95 for oxygen, the value obtained by Keiser[2], we have.

Total wt. of Zinc.	Total wt. of ZnO.	At. wt. of Zn. O = 15·951.
16·13161	20·08608	65·065

[1] Die Atomgewichte der Elemente, p. 13.

[2] American Chemical Journal, Vol. 10 - 249.

These results agree more closely with those of Marignac obtained by the analysis of the double chloride of zinc and potassium and of Van der Plaats obtained by the solution of the metal in acid and measurement of the hydrogen, than with the values determined by any other investigators. A comparison is shown in the following table:

	Marignac. 1st series. (O = 16) 5 experiments	Marignac 2d series (O = 16) 3 experiments	Van der Plaats (O = 16) 3 experiments.	By method here described. O = 16 1 experiment.
Mean	65.29	65.33	65.343.	65.264
Highest	65.[illegible]1	65.[illegible]4	65.[illegible]7	65.[illegible]1
Lowest	65.22	65.28	65.303	65.253
Max. diff.	0.15	0.11	.070	.028

But differences of 7 and 11 hundredths of a unit in a determination of the atomic weight of an element by different methods cannot be neglected as falling within the range of necessary experimental errors.

Admitting equal care and skill on the part of the experimenters, such discrepancies must be ascribed rather to a difference in the inherent difficulties and defects pertaining to the methods themselves. The necessity of effecting the crystallization of the double salt in the presence of an excess of the chloride of zinc, and the difficulty of accurately determining zinc itself, appear to be serious objections to the method of Marignac; and the considerable differences between the results of the individual experiments (0·15 in the first and 0·11 in the second series), indicate that these or other sources of error were of considerable effect. The details of the work of Van der Plaats are not at hand, but the great and well known difficulty of preventing the loss of hydrogen by diffusion and absorption constitutes a general objection to the method which he employed. The objections to the method

Employed in this work will now be considered.

VI.

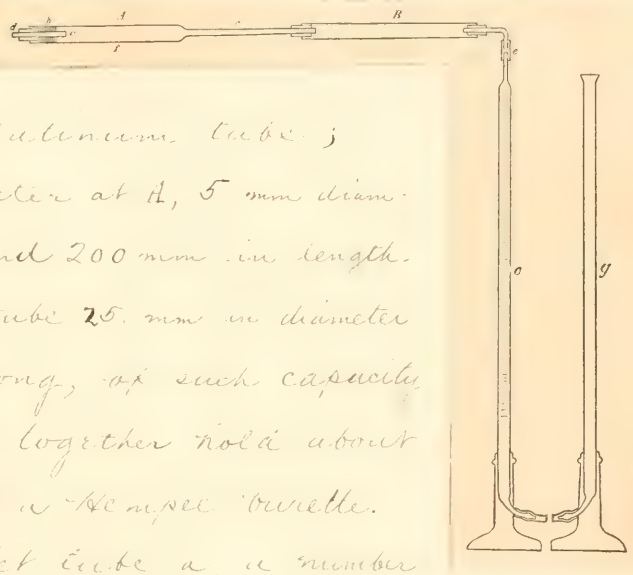
As has already been stated, Marignac has offered two objections to the method here employed for the determination of the atomic weight of zinc. The gradual loss in weight which is suffered when the oxide of zinc is heated in a platinum vessel over a blast lamp, he ascribes to dissociation of the oxide at the temperature attained. But in view of the results of Deville[1] relating to the dissociation of water, and of Deville and Troost[2] relating to the permeability at high temperatures of platinum to hydrogen, it appeared probable that the phenomenon is one of reduction and not of dissociation, that the temperature of the gas flame, in fact, being lower than that at which the

[1] Zeit. Chem. 1863, 24. [2] Zeit. Chem. 1863, 33.

dissociation of water begins, there is in the flame at the same time free oxygen and free hydrogen resulting from the dissociation of water previously formed by the combustion of the gas. The result would be an accumulation of free hydrogen on the inside of any platinum vessel heated in the gas [illegible] of hydrogen through heated platinum.

[illegible] explanation, and make it appear probable that the atmosphere within a platinum vessel heated by such flames as are employed in the laboratory is always a Reducing atmosphere. The method of experimentation consisted in heating with a lamp the air contained in a platinum tube so arranged that the [illegible]

to what extent the oxygen had been absorbed into water. The accompanying figure exhibits the apparatus employed.



A is a platinum tube; 25 mm diameter at A, 5 mm diameter at C, and 200 mm in length. B a glass tube 25 mm in diameter and 150 mm long, of such capacity that A & B together hold about 130 cc; C a Sprengel burette. At the inlet tube a, a number of discs cut from asbestos board and ignited to destroy organic matter, are placed in order to protect the cork d from the heat. The platinum tube is also cooled at the points b and c by wrapping with cloth which is kept wet by means of a dripping arrangement described above. The tubes A and B are

filled with air from the outside of the laboratory, closed at d, and connected at c with the gas burette which was previously full of water. The flame is applied at f. When the air within the tube has attained its maximum expansion, the level of the water in g is adjusted according to the pressure which it is desired to maintain in the apparatus. At the end of each ten minute period of heating, the tube is allowed to cool down in order to facilitate the mixing of the portions of the gas in A, B and C. Finally a small glass tube filled with water and dipping under water in a beaker is attached at d; the gas withdrawn by lowering g and analyzed by the method of Hempel. The substances looked for, and determined when found were carbon dioxide, oxygen, carbon monoxide, hydrogen and nitro-

ity in excess of the quantity normally contained in the air, and was, of course

the basis that we are concerned

Table I.

In Table II. are given the number of cubic centimetres of oxygen burned over in each experiment, also the maximum [illegible] deflexion from the plane into the tube. The calculation is, of course, based on the supposition that the residual [illegible] oxygen originally [illegible] it at 0°.1 is 6 [illegible]

Table II.

	Volume of O_2 lost.	
[illegible]	13·78	[illegible]
[illegible]	14·89	[illegible]
[illegible]	11·46	[illegible]
[illegible]	11·41	[illegible]
[illegible]	10·43	[illegible]
6	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

If we compare the results of Experiments Nos. 1 and 2 with 3 and 4 and with 5

It appears from Exp. 12 that when the oxygen has been reduced to a small quantity, both free oxygen and free hydrogen may exist together in the tube. Experiment No. 9 favour the oxygen, and the fact that the volume did not perceptibly de

[illegible] it was returned to the burette for measurement, appeared to contain a minute quantity of the white clouds which appear when oxygen is absorbed by phosphorous. To settle this question more delicate and greater precautions against possible diffusion of oxygen from the outside will be required. That the quantity of [illegible] is extremely [illegible] because, the tube being hot at the end, the hydrogen passes out of the rear tube with nearly the same facility that it enters in front. Moreover the connections are necessarily such that free hydrogen [illegible]

it; but the supposition that free hydrogen
is accompanied with oxygen, and that
the quantity found afterwards would
be no measure of that which had
diffused into the tube during the experi-
ment, led to the selection of air instead.

These results appear to explain sufficiently
the cause of the constant loss in
weight observed when the oxide of
zinc is heated in platinum over a
gas flame, and to make it extremely
probable that the atmosphere within
any platinum vessel heated by any gas
flame whatever will receive free hydrogen.

They also explain the origin
of those turnishes and sublimates
the analytical chemist so often
on the inside of his crucible after
heating substances supposed to be non-

volatile. Since only the so-called oxidizing portions of the flames were allowed to come in contact with the platinum, the free hydrogen which diffused through the metal must have been produced by the dissociation of water. Whether this dissociation is due solely to the high temperature of the flame or in part to the influence of the platinum itself is a question for further investigation. It appeared not improbable that the very different rates of diffusion of hydrogen and oxygen through platinum at high temperatures may be the cause of the dissociation of the highly heated water vapor, just as different rates of diffusion through liquids of the constituents of some compounds may determine their composition while undergoing solution. [illegible] however indicate that this dissociation of

of the same kind. The crucibles, on
the inside, and the lids, belonging to them, were then heated
for three hours in a muffle furnace
to a temperature sufficient to fuse
commercial ten gram piece of steel

I.

Total gain ooooo1 Total loss

Difference ooooo1 gain.

Series II.

the oxide was heated did not exhibit a trace of the varnish observed by Erdmann[1]. The apparent gain in weight of one one hundredth of a milligram in one case, and the apparent loss of three one hundredths in the other, have of course no significance whatever. They are globules too minute to be detected except when the method of weighing by vibrations is employed and even then they are of very uncertain value.

To test for the presence of the oxides of nitrogen Marignac[2] dissolved the oxide of zinc in hydrochloric acid in the presence of starch and the iodide of potassium. A slight blue coloration was observed, hence he concludes that the oxides of nitrogen must [illegible]. But in order that this test may be relied upon, certain conditions must be fulfilled.

[illegible]

[1] Poggendorff's Annalen 62, 614.

[2] Archives des Sciences Phys. et Nat. (3) 10, 195.

First - The iodide must be free from the iodate of potassium.

Second - The hydrochloric acid must be free from chlorine or any other oxidising agents.

Third - [illegible] must be free from absorbed oxygen.

Fourth - The solutions must be protected from the air.

Whether Marignac observed all these precautions does not appear from his paper. Apparently he must have neglected some one or more of them, since it [illegible] with any sample of the zinc oxide prepared in the manner just described, to obtain the slightest trace of a blue coloration by the method which he employed.

The frequent occurrence of the iodate of potassium in the commercial iodide [illegible]

[illegible] the [illegible]
[illegible] [illegible] [illegible] [illegible] [illegible] [illegible]
the iodometric method, either for quantitative work, or for the detection of oxidizing agents. The fact that so many methods have been devised for the preparation of iodide free from the iodate, and for the removal of the latter from the former, indicates that a simple and effective method for the preparation of the pure iodide of potassium has been much needed but not readily found. The method which was employed for the purposes in this investigation consists in boiling the solution of the iodide of potassium with zinc amalgam. By this means the iodate is completely reduced with formation of zinc hydroxide, and the filtered solution is found to be free from both mercury

and zinc. It is recommended to [illegible] zinc and to have the filter-paper through which the hot solution of the iodide is to be filtered, saturated with [illegible]. The efficiency of the method was tested upon the solutions of pure iodate and bromate of potassium. The [illegible] gram of the iodate dissolved in fifty cubic centimetres of water was completely reduced within forty-five minutes, so that a filtered portion of it gave no blue color when treated with hydrochloric acid and starch paste. In another experiment two grams dissolved in the same amount of water were reduced within one hour and a quarter. One gram of the bromate of potassium was dissolved in fifty cubic [illegible]

and boiled with an excess of zinc [illegible] when complete reduction to the bromide was accomplished.

[illegible] with potassium chlorate, but the zinc amalgam had very little effect upon its solution. A solution of one gram of the salt was boiled for twenty hours with a large excess of the amalgam, at the end of that time only a slight cloud of [illegible] appeared in the solution, and of course examination showed the presence of potassium chlorate.

[illegible] is best prepared by agitating zinc dust [illegible] dilute tartaric acid and washing with water. To remove any chlorine contained in the hydrochloric acid the [illegible] is washed with [illegible].

[illegible] being boiled. The order in which the materials were brought together is as follows: The boiling solution of [illegible] was placed in a Erlenmeyer flask. To this mixture was added, first a considerable amount of the zinc oxide and then the boric acid. The steam rising from the liquid sufficed to protect it from the [illegible]

Investigation of the zinc crystals

Several investigators have studied the crystalline form of zinc both in the elementary state and in alloys, but no very definite results were obtained.

Hogguard[1] obtained crystals of zinc from a furnace slag, which he described as being hexagonal prisms terminated by the basal plane, and streaked parallel to that face. He also mentions having found crystals which were barrel shaped like those of corundum. Nickles[2] examined some crystals of zinc which were obtained by Favre by distillation in a current of hydrogen. He thought them to be pentagonal dodecahedrons such as occur in pyrite and cobaltite, but Gustav Rose[3] subsequently showed that these forms are really aggregates of simple crystals. So far as could be learned from the literature on the subject Rose was the only investigator who attempted

1 - Pogg. Annalen 39, 423. 1836.
2 - Ann de Ch et Ph (3), 22, 31. 1848.
3 - Monatsber. d. K. Ak. July - 1860. Pogg. Ann. Vol. 83, 126.

to measure the crystals and determine their actual crystalline form and axial ratio. He studied the crystals obtained by Nöggerath and, supposing them to be rhombohedral, found the inclination of R to OP in three consecutive zones to be $\left\{\begin{matrix}110° 30'-50\\ 110° 21'-4-\\ 111° 45'-50'\end{matrix}\right\}$. Rose thought it probable that zinc is not only rhombohedral but also [illegible] with [illegible], tellurium and some of the rare metals. He gives the axial ratio $a:c = 1:1.37$ as calculated from his measurements. Stolba[1] obtained from a mass of molten zinc which had been poured out and allowed to flow into a thin layer, crystals consisting of [illegible] bounded by the basal plane, prism and occasionally a steep pyramid. He also speaks of having noticed the "cauliflower shaped crystals" mentioned by Nöggerath.

[1] Jour. für prak. Ch. 46, 175. 1848.

During the distillation of zinc in a vacuum crystals were obtained with planes sufficiently well developed to allow of accurate measurement and it therefore seemed desirable to investigate them with a view to establishing more definitely the crystalline form of the metal. In order to obtain as good crystals as possible the zinc was distilled into the cooler portions of the tube, where it collected in globules which were allowed to cool very slowly - a complete vacuum being maintained in the apparatus until the end of the operation. Four hours were consumed in cooling the distillate from which the best crystals were obtained. The zinc then presented three distinct crystalline forms - first - Aggregates consisting of polyhedral forms having well developed faces which were sometimes striated in various directions showing that they were composed of a number of simple crystals. (Figure I)

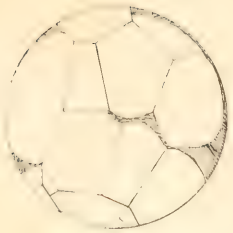


Fig I Aggregate.

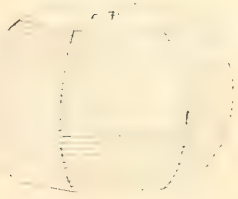


Fig II. Barrel shaped

Secondly - Six-sided barrel shaped crystals having both basal planes well developed, but the pyramidal faces strongly striated by oscillatory combination. (Figure II.)

- Fig III. -

Thirdly - Hexagonal plates having perfect basal cleavage with a strong tendency to grouping in the manner Exhibited in plates of mica (Figure III). This variety had both basal planes and the prism well developed, together with numerous pyramidal faces. It was found to be impossible to obtain good reflections from the striated

pyramidal faces of the barrel shaped crystals, but with the third variety good reflections were usually secured. Six crystals were selected for measurement, four having well developed faces from O to ∞P, while one exhibited both basal planes and the intervening prisms and pyramids. Upon examination it was found that one particular pyramid predominated in all the crystals. A large number of measurements of the inclination of this face to the basal plane yielded the average number 57°27', and if this face be taken as the unit pyramid, the axial ratio would be a : ć = 1 : 1·35642 The angles of inclination of four other pyramids were measured and their indices calculated from the axial ratio just given. The following table shows the observed and calculated angles for each face. The number given for a particular face of each crystal is an average of several distinct observations made

on the different zones of that crystal. The number of observations from which each average is calculated, is inclosed in parenthesis after that average.

Table I.

Crystal.	$\frac{4}{3}P$	$\frac{2}{3}P$	P	$\frac{3}{2}P$	$6P$	∞P
I.	41°49′ (1)	——	——	——	——	——
II.	41°19′ (2)	46°36′ (3)	57°28′ (3)	——	84°3′ (2)	90°2′ (1)
III.	——	46°00 (1)	57°26′ (3)	——	——	——
IV.	——	——	57°13′ (4)	66°42′ (1)	——	89°52′ (1)
V.	42°00 (1)	46°45′ (1)	57°42′ (4)	——	83°18′ (1)	89°52′ (2)
VI.	41°16′ (1)	46°58′ (1)	57°14′ (4)	66°31′ (1)	83°06′ (1)	89°56′ (1)
Mean	41°36′	46°37′	57°27′	66°18′	83°44′	89°55′
Calculated	41°50′	46°14′	57°27′	66°57′	——	90°
Difference	0°14′	0°23′	0°00′	0°39′	0°12′	0°05′

In five crystals the angles between the contiguous unit pyramid faces were measured, and the axial ratio calculated independently of the previous measurements. The results are given in Table II.

Table IV.

no. of Crystals	PAP Zone I.	PAP Zone II	PAP Zone III	PAP Zone IV	Averages
III	[illegible]	[illegible]		[illegible]	[illegible]
IV	49°38′	49°24′	50°27′	49°31′	49°44′
				Mean	49°43′

Calculating the axial ratio from this num-
[illegible] a : c 1 : 1·3447

From these results it appears that zinc is holohedral and crystallizes in the hexagonal system. But the results here obtained do not agree with those obtained by Rose, and it does not seem probable that zinc is rhombohedral like Arsenic, Antimony, Bismuth and [illegible] although its axial ratio is [illegible] near [illegible] these isomorphous elements as shown below

Arsenic - a : ċ 1 : 1·3779
Antimony - a : ċ 1 : 1·3068
Bismuth - a : ċ - 1 : 1·3035
Tellurium - a : ċ = 1 : 1·3302
Zinc - a : ċ - 1 : 1·3564

} [illegible] in hexagonal pinakoids have many of the characteristics of which crystals, as shown

on the grouping parallel to the basal plane, the perfect basal cleavage, and from the fact that zinc shows a very excellent percussion figure, with the rays of the star parallel to the pyramidal edges, when a cleavage plate of it is struck with a needle point.

[redacted] undertaken by the writer under the direction and with the generous cooperation of Dr. G. H. Williams, and he takes this opportunity to thank him for the valuable assistance thus rendered.

In closing this dissertation the writer takes great pleasure in expressing his sincere thanks to Professor Remsen for the instruction received from him both in the lecture room and in the Laboratory; and he would further express his deepest gratitude to Dr. H. N. Morse, to whose direction and earnest cooperation the satisfactory completion of this investigation is due.

Biographical Note

The writer of this dissertation was born in East Cleveland, Ohio, Nov. 17th. 1863. His early schooling was received at Shaw Academy, Cleveland, Ohio. He prepared for College at the East Cleveland High School, [illegible] College at [illegible] University in the year 1882 and graduated with the degree of Bachelor of Arts in June 1886; in the Autumn of the same year he entered the graduate department of the [illegible] University, [illegible] pursuing [illegible] studies.